Appendix B
Testing Polyaluminum Chloride

APPENDIX B

Testing Polyaluminum Chloride

B.1 Introduction

During the October 14, 1999 SRP conference call, a switch to polyaluminum chloride (PACL) from aluminum sulfate was discussed, because of the relationship between sulfate loading and mercury cycling. The mercury issue in the Everglades has and continues to get detailed scrutiny. Because of the complexity and cost of the technical issues it is unlikely that the sulfate question will be answered in the near future, thus a cloud of uncertainty is likely to remain if alum is used.

Sulfate loading is a concern because of the link of sulfur cycling in wetland environments with microbially mediated methylation of mercury. Methylmercury is highly toxic, it is produced in sediments under microbial action by sulfur reducing bacteria. Once formed methylmercury can bioaccumulate in higher trophic levels of the food chain, such as largemouth bass for example. Toxicity problems for humans can arise through ingestion of animals that have bioaccumulated methylmercury. As noted in the Everglades Interim Report (EIR) (SFWMD, 1999) and the Everglades Consolidated Report (ECR) (SFWMD, 2000)water quality can effect mercury transformations, such as methylation, and therefore the potential for bioaccumulation. It is suggested that sulfur concentrations control the rate of methylmercury production; the EIR and ECR suggest that pore water sulfide concentrations may be a strong predictor of methylation rates and methylmercury concentration.

There is much that is uncertain about the chemical and biological mechanisms of mercury cycling and methylation, and the role sulfate plays is not clearly established. In addition, the uncertainty is unlikely to be resolved anytime soon, thus downstream sulfate loading could cast the project in a negative light. The sulfate/methylation issue led to a discussion of alum substitutes.

The discussion of alternatives to alum concluded with the following points:

- Alternative aluminum coagulants include polyaluminum chloride (PAC) and sodium aluminate
- In terms of TP removal capability alum and PAC are expected to be similar
- Bench-scale testing of PAC on ENR water would be needed
- In terms of equipment procurement, the chemical feed system for treatment units is likely to be flexible enough for use with either chemical.

B.2 Objectives

The intent of prescreening testing was to compare several poly-aluminum chloride coagulants (PACL) to alum (aluminum sulfate) and determine the starting condition for pilot testing. The objectives of testing were:

- Verify coagulant effect on pH
- Verify coagulant dosage relationship on residual P and residual soluble aluminum
- Select appropriate PACL product and starting dosage for use at the pilot-scale
- Select the appropriate flocculation polymer(s) and starting dosage for use at the pilot-scale

B.3 Standard Testing Procedures

B.3.1 Feedstock Collection

Samples representative of Everglades Agricultural Area (EAA) effluent were collected from the feed reservoirs at the North and South ENR test sites. To ensure fresh samples after collection water was immediately transported to the UCF-ESEI laboratory where it was stored until use in a walk in refrigerator at 4 ^{O}C. Samples were collected using a centrifugal pump, with the suction line submerged approximately 2 feet below the surface of the reservoir at the vicinity of the bar screen. Samples were stored in 5-gallon polyethylene carboys. The carboys were rinsed three times with the sample solution before sample collection. Samples drawn from the north ENR site are referred to as NEAA. Samples drawn from the south ENR site are referred to as SSTA. Samples not needed immediately were stored in a walk-in cooler at the UCF-ESEI Laboratory. Samples used within 24 hours of collection were stored in the lab and allowed to warm to room temperature.

An initial and final influent composite of the NEAA water was analyzed for pH, TP, TDP, dissolved orthophosphate, alkalinity, turbidity, color, and dissolved aluminum. Since only a single day screening of SSTA waters was conducted using PACl, only the initial raw water sample was submitted for the same parameters.

B.3.2 General Jar Testing Procedure

Testing followed procedures described by Hudson and Wagner (1981) for conventional jar testing. Before testing, the raw water samples were titrated with the coagulants and acid to determine alkalinity and the acid/base requirements for each specific jar.

Filling

Two-liter square beakers were used with a standard six-place Phipps and Bird gang stirrer. The feedstock carboy was mixed and the test beaker(s) filled to the 1-liter mark. The feedstock carboy was then remixed and the volume of the beakers raised to the full 2-liter mark.

Dosing

Rapid mixing was conducted at 200 revolutions per minute (rpm) ($G > 200s^{-1}$ in square 2-liter beakers). At zero seconds, the primary coagulant was added at the tip of the mixer blades with a micro-syringe. Immediately thereafter, a predetermined amount of acid or base was added to achieve the desired pH setpoint by using a volumetric pipette or syringe to deliver the appropriate volume at the tip of the mixer blades. The anionic flocculant was added next and rapid mixing continued for 15 seconds.

Flocculating

The mixing speed was reduced to 34 rpm (G = $23s^{-1}$ in square 2-liter beakers) 15 seconds after the polymer was added. This provided an appropriate energy to form and uniformly suspend particles throughout the flocculation period. The sample was allowed to flocculate for 20 minutes. The pH was adjusted during the flocculation period when necessary.

Settling and Sampling

Samples of treated water were withdrawn from the sampling port located 10 cm below the initial liquid surface. Filtered or dissolved sample fractions were prepared by using a peristaltic pump and 0.45-micron membrane filters.

B.3.3 Solids Contact Simulations

A solids contact simulation was performed with the coagulant dosage and the optimized polymer and dosage determined from the previous testing. This set of tests allows a qualitative assessment of the solids characteristics, as well as an opportunity to verify residual P and metal concentrations after treatment.

Solids contact was simulated by running sequential jar tests while retaining the sludge produced from previous tests. The estimated hydraulic retention time (HRT) of liquid in the pilot reactors is expected to be approximately 2 hours. Assuming a minimum target solids retention time (SRT) of 1 day, the number of batches needed to fully simulate pilot operating conditions was calculated as SRT divided by HRT. Therefore, 24 hrs divided by 2 hrs equals 12 batches.

Two beakers were utilized for each source water/coagulant combination tested. While one beaker was in a rapid mix (reaction) and flocculation cycle, the other beaker was in a settling and decant cycle, so that the solids from the settled beaker were ready to be added to the next reaction beaker. The bottom 400 milliliters (mm) of sample from each previous jar test was returned to the subsequent jar test during the flocculation period.

Rapid mixing for the addition of chemicals followed the same procedure outlined previously as part of the standard jar test procedure. Raw influent (1.6 liters) reacted through rapid mix using the optimum coagulant dose, pH, and polymer dose determined previously. The bottom 400 m of liquor from the previous jar test was then carefully added at the start of the flocculation period. Flocculation proceeded for 20 minutes, and settling continued for a period of 10 minutes.

Solids settleability and supernatant quality were measured after flocculation of the fourth, eighth, and twelfth batches. At each of these intervals, supernatant samples were collected from the sample port 1, 2, 5, and 10 minutes after settling commences. These samples were analyzed for turbidity. Both the raw influent sample and the sample collected at 5 minutes after settling for the twelfth batch was analyzed for TP, TDP, dissolved ortho phosphate, residual dissolved metal, and color. Sludge volume (m/L) after 30 minutes of settling was recorded, and total sludge production was measured as TSS. One solids contact test was conducted.

B.4 Results and Discussion

The following section presents the results of the prescreening testing of PACL and flocculation aids. Properties of the alum, four PACL coagulants, and an iron coagulant evaluated during this testing and associated published information are presented in Exhibit B-1. Properties of the five flocculation aids and the published information are presented in Exhibit B-2.

Exhibit B-1.
Coagulants Evaluated During Testing

Company	Coagulant	Percent Aluminum	Specific Gravity	Percent Basicity
Kemwater	PAX-18	9	1.37	41
	PAX-XL19	12.4	1.34	80
	AK-2000	12.4	1.33	80
	Ferric Chloride	13.9*	1.43	Acidic
General Chemical	Hyperion-1090	12.3	1.37	78
	Alum	4.4	1.335	Acidic

* Percent as Fe^{+3}

EXHIBIT B-2.
Flocculation Aids Evaluated During Testing

Company	Name	Relative Molecular Weight	%Charge	% Active Ingredients	S.G.
Cytec	N-1986	Medium	0	25	1.0
	A-1849RS	Medium	3	25	1.0
	A-1883	High	30	28	1.0
	A-130	High	35	80	Dry
	A-130hmw	Very High	35	80	Dry

B.4.1 Coagulant effect on pH

This section presents the effects of increasing doses of coagulant on finished water pH. This testing was conducted to determine what quantities of acid or base should be added during jar testing, and to produce insight in to quantities needed for pilot studies. The testing procedure consisted of measuring the pH of a 2-liter aliquot of north Everglades Agricultural Area (NEAA) water while the dose of coagulant was increased.

PACL is a prepolymerized inorganic aluminum coagulant that is not described by one chemical formula such as alum and is proprietary in nature. However, one descriptive characteristic of PACL is the percent basicity, which is the degree of neutralization or the replacement of chloride ions with hydroxide ions. Essentially the higher the percent basicity the less effect the coagulant will have on depressing the pH of a given water.

Exhibit B-3 presents the titration curves for two of the PACL coagulants and alum. Alum can be considered an acid and thus reduced the pH the greatest with increasing dose. Alum requires base addition to maintain the pH above the minimum target of pH 6.5 at doses above 2.25 meq/L Al (20 mg/L Al) for the water tested. PAX-18 had the lowest basicity of approximately 41 percent and did not depress the pH below the minimum target range until a dose of 4 meq/L Al (36 mg/L Al). Hyperion-1090, which has a basicity of 73 to 83 percent had minimal effect reducing the natural water pH by approximately 0.4 units for the range of doses evaluated.

Based on these results the indication is that PACL products with percent basicity above 40 percent will not require the addition of acid or base to control the pH within the natural water range. It should be noted that major changes in the natural water alkalinity or buffering capacity will vary the process pH using any of these coagulants. However, the pH is effected less with the use of PACL.

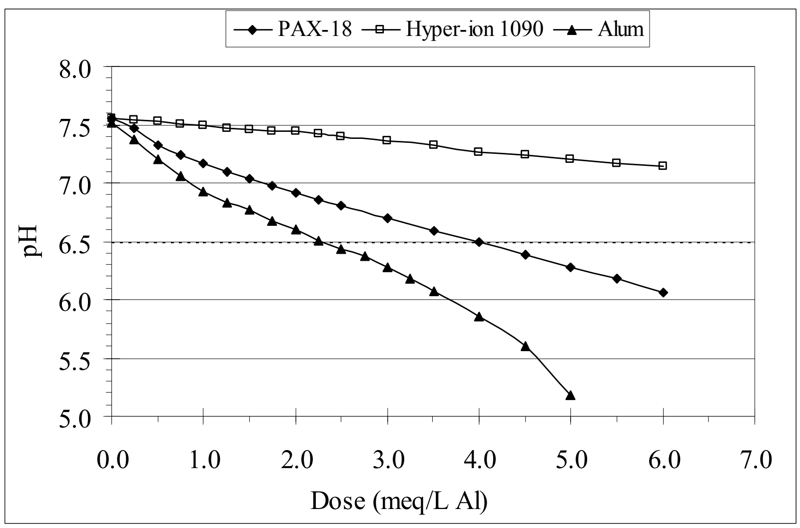

EXHIBIT B-3
Effect of Coagulant Dose on pH of NEAA Water

B.4.2 Coagulant and Dose Selection

The coagulants were dosed at concentrations ranging from 0.5 to 2.5 meq/L as Al. The A-1849RS flocculation aid was added at a dose concentration of 0.5 mg/L. The pH of the reactions after settling was verified to be in the range of natural waters and are presented in Exhibit B-4. To maintain the pH of the alum coagulation reaction above 6.5 when dosed at 2.5 meq/L, sodium hydroxide was added at a concentration of 0.5 meq/L. The PACL coagulants did not require any pH adjustment.

Samples were collected after settling and analyzed for total dissolved phosphorus (TDP), dissolved aluminum, turbidity, and color analysis. With the exception of turbidity the samples were filtering through a 0.45-micron filter cartridge prior to analysis. The TDP for each coagulant and dose is presented in Exhibit B-5. The raw NEAA water TDP was measured at approximately 120 ug/L P. The coagulants produced the general trend of increased TDP removal with increasing dose. The Hyperion-1090 and AK-2000 PACL products produced the lowest TDP results in the dose range of 1.5 to 2.0 meq/L, which was similar if not better than the alum results which reduced the TDP down to approximately 20 ug/L P.

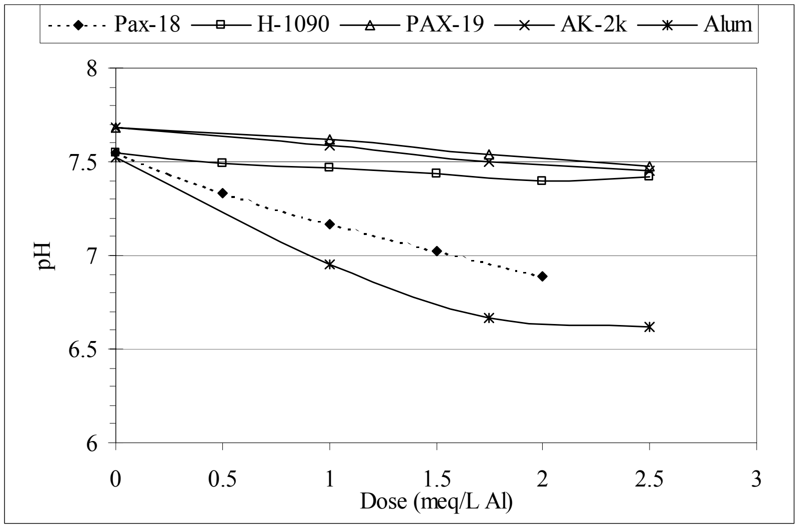

EXHIBIT B-4
Reaction pH as a Function of Coagulant and Dose

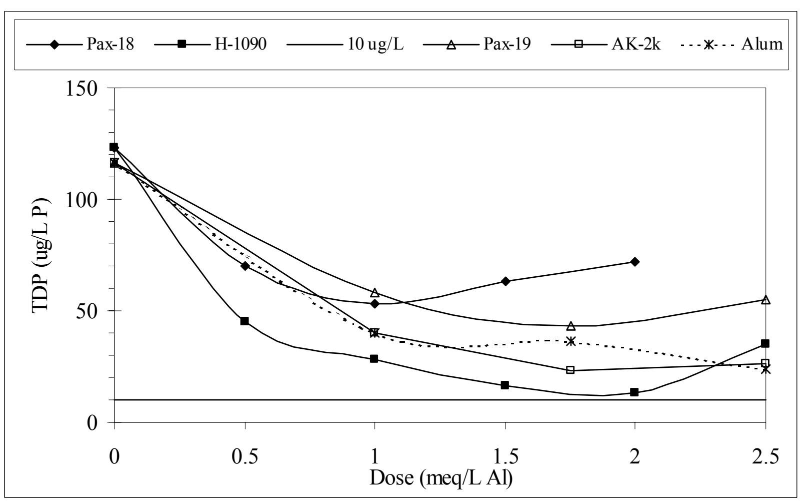

EXHIBIT B-5
Total Dissolved Phosphorus as a Function of Coagulant and Dose

The dissolved aluminum results are presented in Exhibit B-6. The results obtained from the testing of PAX-18 and Hyperion-1090 were significantly higher than later testing using alum, PAX-19 and AK-2000. Initially PAX-18 and Hyperion-1090 were tested with sampling and analysis conducted together. After the initial testing with PAX-18 and Hyperion-1090 was conducted, another round of testing was conducted using fresh coagulants after they were received. Another aliquot of the NEAA raw water used for testing was analyzed with the second set of jar test samples and resulted in a lower dissolved aluminum residual. The NEAA raw water dissolved aluminum dropped from a duplicated 360 ug/L to the analytical detection limit of 2.5 ug/L. The significant drop in dissolved aluminum concentrations between the two sets of testing is not readily explainable. However, the relative increase in residual aluminum associated with the coagulant Pax-19, AK-2000 and Hyperion-1090 was small and minimized in the range of 1.5 to 2.5 meq/L Al.

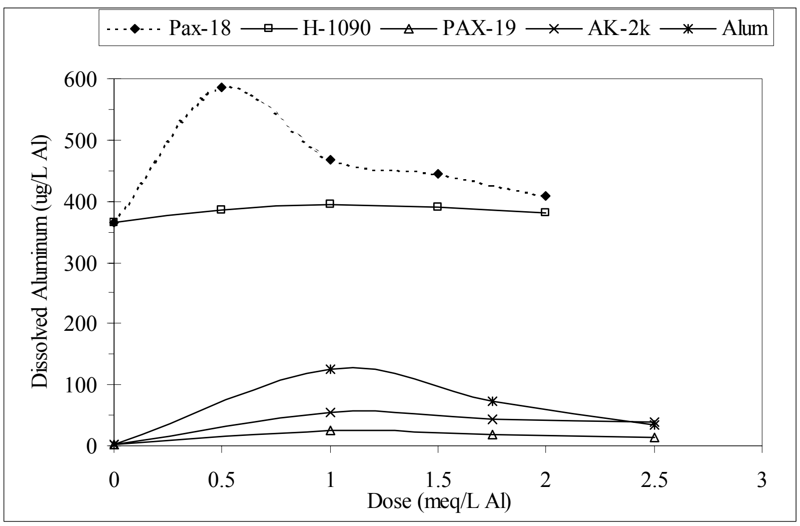

EXHIBIT B-6
Dissolved Aluminum Residual as a Function of Coagulant and Dose

The color of the raw NEAA and filtered water for each coagulant and dose was measured in the lab to gain a more rapid insight on the trend of the coagulation process. The results of color analysis are presented in Exhibit B-7. The trend as expected is that the finished water color decreases with increasing coagulant dose and produced relatively smooth curves with no indication of anomalies. The raw water filtered color was approximately 140 CPU and was reduced to approximately 40 CPU at a coagulant dose of 1.5 meq/L Al. The coagulants followed historical trends and performed similar with respect to color removal on an equivalent aluminum basis.

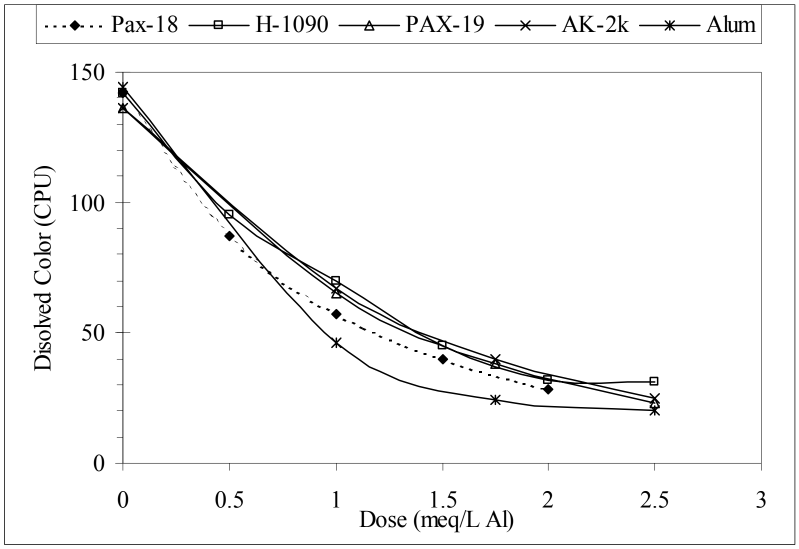

EXHIBIT B-7
Dissolved Color as a Function of Coagulant and Dose

Turbidity was measured for each coagulant and dose at 5 minutes of settling after the flocculation period ended. The analysis represents the relative ability of the solids to settle at a corresponding surface loading rate (SLR) of 0.5 gpm/sf. The results of the turbidity analysis are presented in Exhibit B-8. The results show a characteristic initial increase in turbidity with coagulant dose to approximately 1 meq/L after which there is a decline with increasing dose. With the exception of Hyperion-1090 the results indicate that the coagulant and polymer dose combinations were similar and produced better solids settling at coagulant dose concentrations above 1 meq/L as AL. The high turbidity associated with the Hyperion-1090 doses of 1.5 and 2.0 meq/L are suspected to be anomalous in light of subsequent testing.

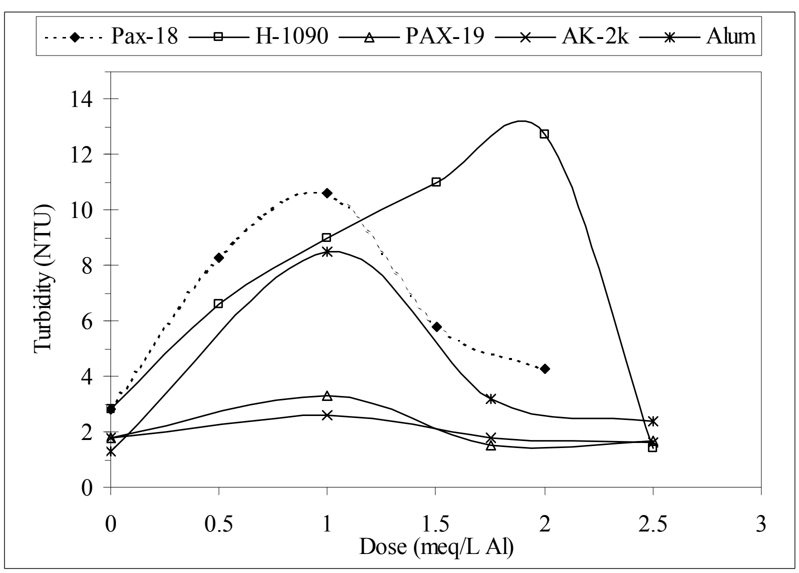

EXHIBIT B-8
Turbidity at SLR 0.5 gpm/sf as a Function of Coagulant and Dose

Because of the comparable results to alum and the advantage of using different manufacturers, Hyperion-1090 and AK-2000 were selected for further testing. Based on TDP and residual aluminum results a PACL dose of approximately 1.5 to 1.75 meq/L as Al should be used as an initial starting point for the pilot study.

B.4.3 Polymer Selection

The following section presents the results of polymer screening and selection testing. The flocculent aids along with the published manufacturer specifications were previously presented in Exhibit B-2. For screening purposes 5 flocculation aids were used with the PACL coagulant AK-2000 for treating the NEAA water. The flocculent aids were evaluated at doses of 0.25, 0.5 and 0.75 mg/L with the coagulant dose held constant at 1.75 meq/L Al. A summary of the screening results using a flocculent aid dose of 0.5 mg/L, which was found to produce the best results, is presented in Exhibit B-9. With the exception of the A-1883 polymer all flocculent aids performed well at the 0.5 mg/L dose producing settled water turbidities below 2 NTU at the standard 0.5 gpm/sf SLR. The non-ionic N-1986 polymer produced the lowest turbidities at SLRs below 1.2 gpm/sf.

The N-1986 and A-130 flocculent aids were evaluated with the coagulants ferric chloride and Hyperion-1090 to verify if acceptable settling could be achieved. The objective was to identify one polymer that could be used with the different coagulants selected for pilot study. The settled water turbidity for varying SLR is presented in Exhibit B-10. The N-1986 and A-130 flocculent aids were dosed at 0.5 mg/L and the coagulants ferric chloride and Hyperion-1090 were dosed at 1.75 meq/L. Results indicate that the N-1986 nonionic polymer produced the lowest settled turbidity for both coagulants at SLR below 1.2 gpm/sf.

The N-1986 polymer produced the best settled turbidity results and is recommended for use in the pilot studies. With a coagulant dose of 1.5 to 1.75 meq/L the recommended polymer dose is 0.5 mg/L as active ingredient.

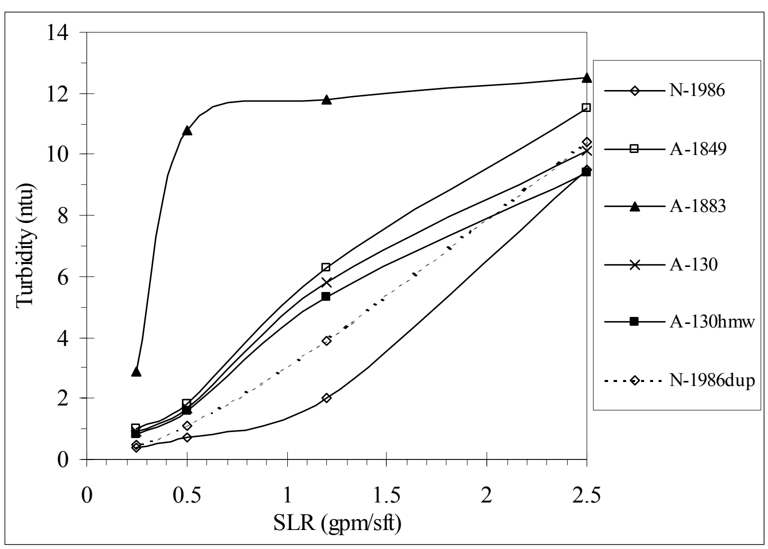

EXHIBIT B-9
Settled Water Turbidities for Polymer Selection Using PACL AK-2000

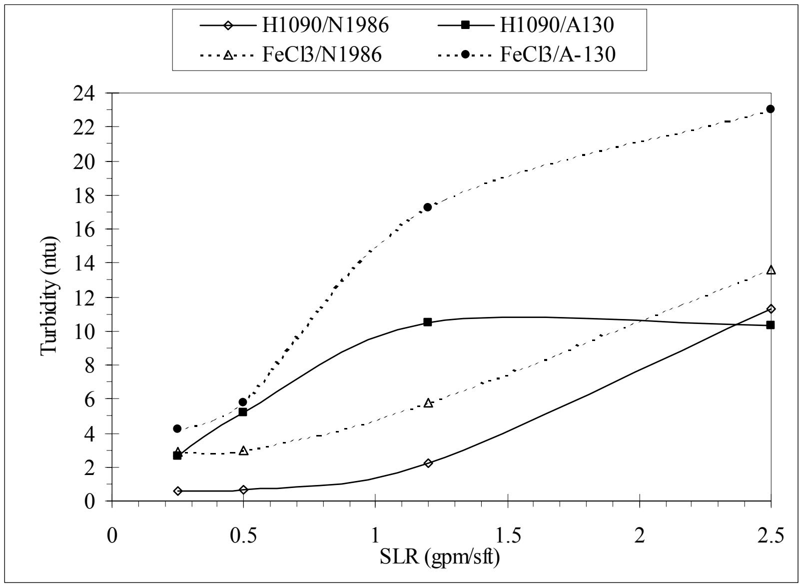

EXHIBIT B-10
Settled Water Turbidities For Polymer Selection Using Hyperion-1090 and Ferric Chloride

B.4.4 Selected PACL Coagulants and Polymer Comparison

The following section presents the results of analysis conducted on the coagulants and polymer combinations selected for use during the pilot studies. Aliquots of NEAA and SSTA waters were treated with the PACL coagulants, AK-2000 and Hyperion-1090. The coagulants were dosed at a concentration of 1.75 meq/L in combination with the N-1986 polymer at a dose concentration of 0.5 mg/L.

Samples were collected at 5 minutes and measured for turbidity to verify settling characteristics. The results of the turbidity analysis are presented in Exhibit B-11. The raw water turbidity for the NEAA and SSTA were 2.7 and 2.5 ntu, respectively. The Hyperion-1090 settled slightly better than the AK-2000 when treating the NEAA water at 0.8 versus 1.0 ntu. However, the trend was reversed when treating the SSTA water and the relative difference can be considered insignificant.

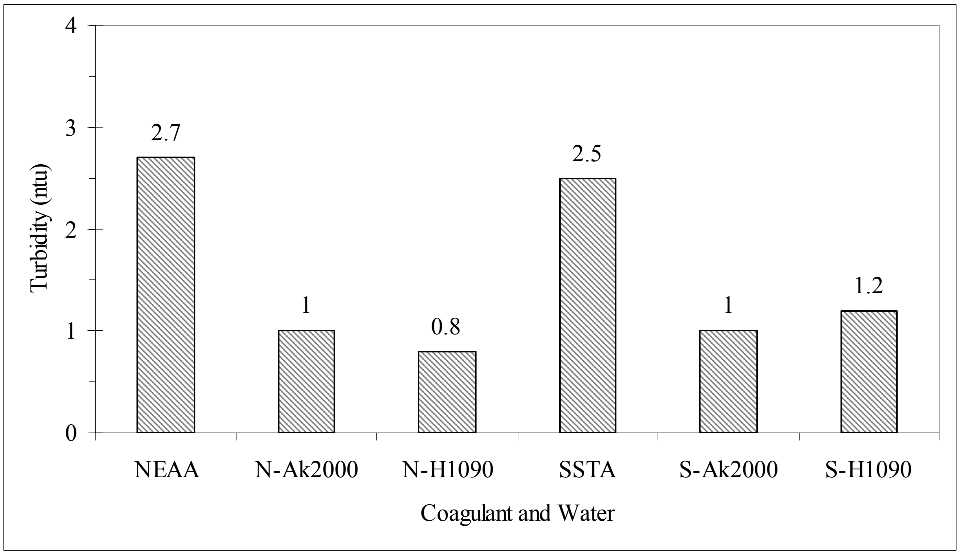

EXHIBIT B-11
Settled Water Turbidity at SLR 0.5 gpm/sf

After 10 minutes of settling samples were collected for total phosphorus, total dissolved phosphorus and dissolved aluminum. The total phosphorus (TP) and total dissolved phosphorus (TDP) results are presented in Exhibit B-12. The results show that the TP of the raw SSTA water ranges from 66 to 121 ug/L P and the NEAA water was measured at 133 ug/L P. The TDP concentration of the SSTA water was less than the NEAA water at 27 versus 51 ug/L P, respectively. The coagulation processes produced mixed results with the AK-2000 performing the best on the NEAA water while the Hyperion-1090 performed the best on the SSTA water. The AK-2000 reduced the NEAA water TP concentration by 65 ug/L P or 51 percent but only reduced the TDP by 9 ug/L. The NEAA water treated with Hyperion-1090 increased the TP and TDP by 20 and 25 ug/L P, respectively. However, the Hyperion-1090 reduced the SSTA TP and TDP down to approximately 17 ug/L P. The AK-2000 coagulant increased the TP and TDP by 43 and 74 percent, respectively. These results indicate that a reduction in TP and TDP can be achieved using PACL and that for initiating the pilot studies either coagulant could be used.

The results of residual dissolved aluminum analysis are presented in Exhibit B-13. The results show that the dissolved aluminum in raw NEAA and SSTA water were measured at approximately 13 ug/L. The coagulation process using either PACL increased the dissolved aluminum by 46 to 56 ug/L Al. The relative difference between the PACL coagulants is insignificant and either coagulant could be used to initiate pilot studies.

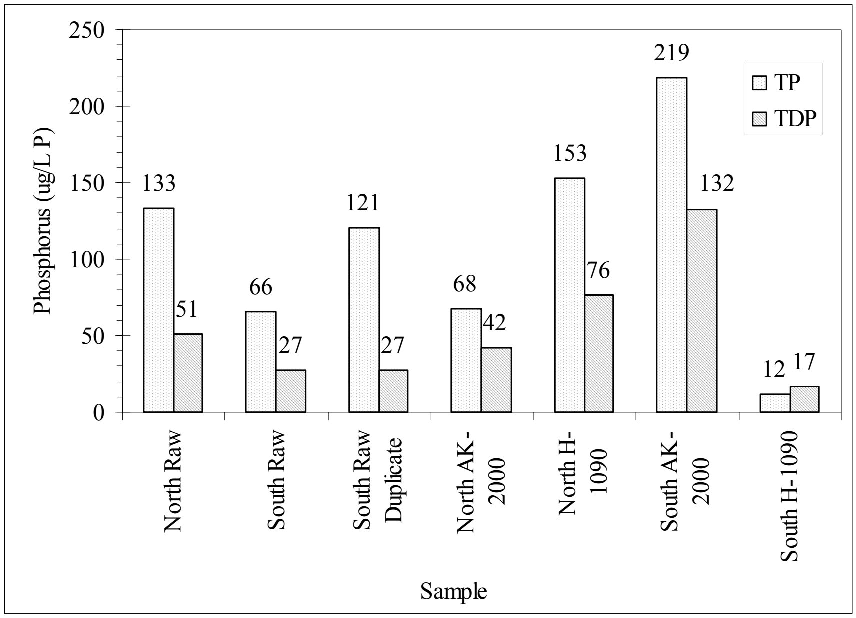

EXHIBIT B-12
Total Phosphorus and Total Dissolved Phosphorus Concentration for PACL Comparison

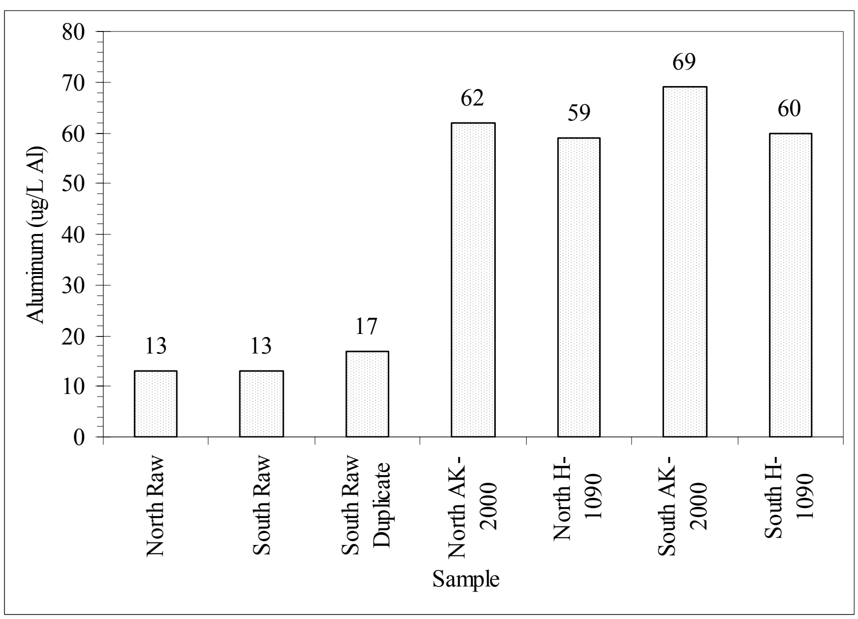

EXHIBIT B-13
Dissolved Aluminum Concentrations for PACL Comparison

B.4.5 Quality Control and Quality Assurance

The following section presents a summary of duplicate samples and phosphorus analysis of the chemical used in the jar testing. Exhibit B-14 presents an initial TP analysis of chemical used in this jar testing or planned for use in pilot studies. For this set of analysis reagent grade de-ionized (blank) water was dosed at a concentration of 1 meq/L of chemical. The utility of this analysis is that the addition of TP from the chemical addition can be calculated by multiplying the value report in Exhibit B-14 by the dose of chemical used in meq/L. The reagent grade water had a reported TP concentration of 4 ug/L. However, one of the alum split samples (i.e. one sample is split into two for analysis) was reported at 3 ug/L or less than the water used to dilute it. The second alum split sample was reported at 15 ug/L P. The concentration of TP in the chemical ranged from 8 to 100 ug/L P with the PACL coagulants PAX-18 and AK-2000 containing the greatest concentrations.

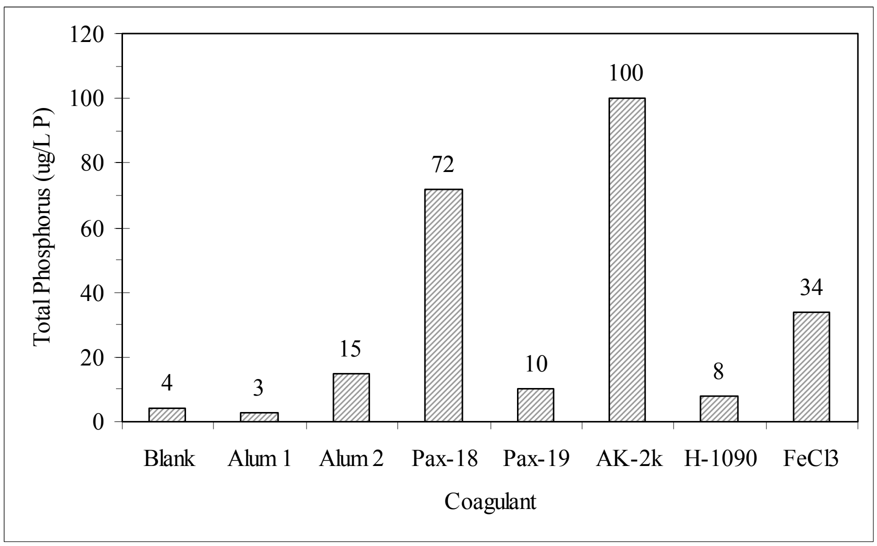

EXHIBIT B-14
Total Phosphorus Measured In Process Chemicals per 1 meq/L Dose

A second set of analysis was conducted on chemicals used or proposed for use to determine the amount of TP that is particulate in nature. The TP and TDP concentration measured in the process chemicals after they were diluted to a concentration of 1 meq/L are presented in Exhibit B-15. The results indicate that the dilution water (blank), sodium hydroxide, Hyperion-1090 and the Kemiron ferric chloride have TP and TDP at or near the analytical detection level of 4 ug/L P. The AK-2000 and to a lesser extent Aguakem ferric chloride show higher concentrations of both TP and TDP.

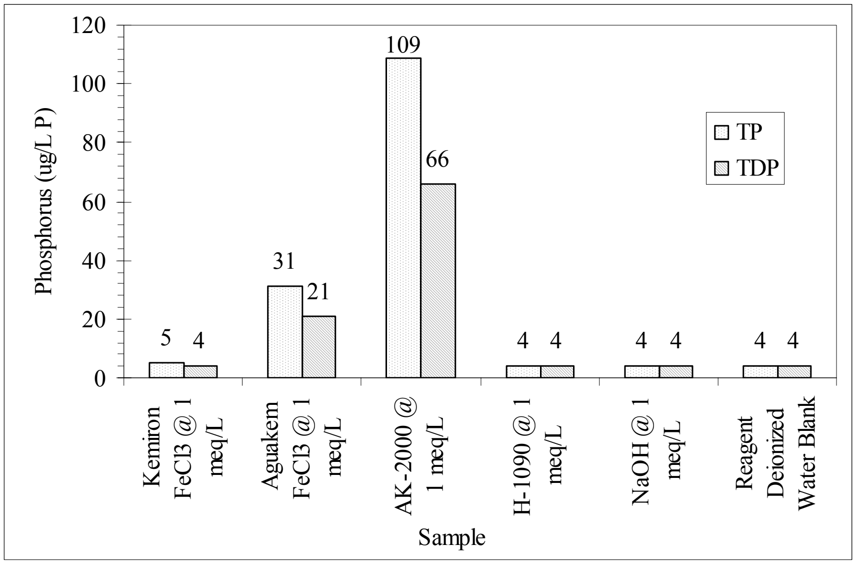

EXHIBIT B-15
Total Phosphorus Measured in Process Chemicals per 1 meq/L Dose

The duplicate samples submitted to the laboratory for analysis are presented in Exhibit B-16. The results listed in rows represent one sample that was split into two aliquots and submitted separately to the laboratory for analysis. For instance the first NEAA sample was an aliquot from the specific carboy used for testing that day split into two bottles, preserved and ship to the laboratory as a blind duplicate (i.e. the laboratory did not know it was a duplicate). The results for this particular analysis were not very consistent with over 115 percent difference. However, the aluminum residual was relatively consistent at 366 and 360 ug/L. Samples with the same identification such as the NEAA and blanks were aliquots associated with a different day of testing. Over all the analysis was relatively good, however there was enough variability that reliance on the absolute value could be suspect and therefore the selection process was made based on the relative difference of the chemicals tested and trends observed.

EXHIBIT B-16
Duplicate Sample Analysis

Sample ID	TDP (ug/L P)		Dissolved Al (ug/L)	
	1	2	1	2
NEAA	123	57	366	360
NEAA	116	94	<2.5	<2.5
NEAA	51		<2.5	
NEAA			<13	
SSTA	27	27	<13	<17
I-1.0	28	28		
X-1.0	98	53		
A-1.75	50	36	71.9	92.4
L-2.5	78	55	14.2	17.2
Blanks	<4	7	<2.5	<2.5
Blanks	<4	47	<12	<12
Blanks	<4	<4		
AK-2000	100	109		
H-1090	8	<4		
Aguakem FeCl3	34	31		

*Diluted to 1 meq/L

B.5 Conclusions and Recommendations

B.5.1 Conclusions

- PACL coagulants with percent basicity of 78 percent or higher (Hyperion-1090 and AK-2000 did not require the addition of acid or base to control pH in the natural water range.
- The Hyperion-1090 and AK-2000 coagulants reduced total dissolved phosphorus as well as alum.
- The N-1986 flocculation aid was the most effective polymer tested for enhanced settling.

B.5.2 Recommendations

- Either of the PACL coagulants, Hyperion-1090 or AK-2000 can be used to initiate the pilot studies.
- The initial PACL dose should be 1.5 to 2.0 meq/L Al.
- The use of sodium hydroxide for pH control should not be required, however it should be available should major reductions in raw water buffering capacity occur.
- The N-1986 flocculation aid should be used for enhanced settling
- The N-1986 polymer should be dosed initially at a concentration of 0.5 mg/L active ingredient.